

# Use of Zinc Amalgam in the Evolution Method for Determination of Sulphur in Iron and Steel.

By

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The evolution method as a way of determining sulphur in iron and steel is much appreciated in technical practice by reason of its being simple and much quicker than the gravimetric (barium sulphate) method. Reproaches have, however, been often raised against the unreliability of the process, which is said to give too low percentages for sulphur. It is true that the process has defects in its fundamental principles, inasmuch as the states of sulphur in iron and steel are varied and so not necessarily destined to give hydrogen sulphide on being treated with hydrochloric acid. In fact, some might remain unaffected, some be changed into organic sulphides. Furthermore, a solution of hydrogen sulphide is liable to be oxidised into sulphuric acid on coming into contact with oxygen kept in solution or in the air. It may also liberate sulphur on being brought into reaction with ferric chloride in solution. In spite of such differences of conditions, we are usually in the habit of using this method with no care for any of them, and this must be one reason why the results lack accuracy.

We shall now see, therefore, what would be the real states of sulphur in iron and steel and consider the best means to meet them as well as other difficulties associated with the method.

Sulphur combines with iron to form the sulphide, which may exist either in isolated crystals uniformly distributed or segregated from it, or in a solid solution, which is likely to be the case when the molten metal is too rapidly cooled. Under such different states of existence, the action of hydrochloric acid can never be the same. First of all, if the acid is dilute, the rate of evolution<sup>1</sup> of hydrogen sulphide must be slow and lead to its easier oxidation, whereas the formation of organic sulphides would be much greater. If, on the contrary, the acid be stronger, the rate of evolution will be greater and naturally prevent oxidation of hydrogen sulphide. Yet even in that case, we might suspect some of the sulphur in solid solution would not be converted into hydrogen sulphide but be separated rather as free sulphur. As a remedy for the latter difficulties, it has been the habit to anneal the material before it is subject to analysis. A similar instance perhaps may occur, too, after the effects of ageing upon steel. These effects are indeed nothing but the oxidation of samples and must tend to keep the sulphur partly as sulphates and partly in the free state. They would, therefore, be cancelled, as is generally known, by reheating the materials with carbon at high temperatures. However effective be each of the pre-treatments, so far as they are not unified, the evolution method would be a little too troublesome. Moreover, the use of too strong acid can not be held as convenient on several grounds.<sup>2</sup> We shall now remark, too, that the Bureau of Standards, U. S. A., is also of opinion, that the results of the evolution method are too low, the data for which are to be given later on.

According to my experience, all these difficulties can, however, easily be overcome by making use of the stronger acid, sp. gr. 1.15–1.70, in presence of zinc amalgam. Vivid evolution of hydrogen will on the

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<sup>1</sup> For the influence of the rate of evolution on the production of hydrogen sulphide, see Matthewman: *West of Scotland Iron and Steel Institute*, Session 1896–97.

<sup>2</sup> Bauer and Deiss, *Analyse von Eisen und Stahl*, 2nd. Ed., p. 210.

one hand keep hydrogen sulphide from oxidation, and on the other reduce the liberated sulphur or sulphuric acid into hydrogen sulphide, whereas the formation of organic sulphides would mostly be prevented thereby. The use of tin and hydrochloric acid as recommended by Treadwell<sup>3</sup> cannot excel my process, because we have in our case not only a steady vivid evolution of hydrogen but also mercury reduced serving as a catalyser for the intended reactions.

As to the concentration of the acid, in so much as there is zinc amalgam in addition to the samples, it is obvious that we want more of it, so that we may use it in a concentrated state in order not to have the liquid in the gas generator too bulky. Fumes from such a stronger acid can easily be caught by placing a wash-bottle next to the generator. The following is a full description of my modification.

#### **REAGENTS.**

1. Hydrochloric acid : sp. gr. 1.20.
2. Zinc amalgam : about 8 gr. pure crystallised mercuric chloride mixed with about 1/2 kg. pure zinc in grains of 2-3 mm. sizes, covered with water, shaken till the reaction is over, well washed with dilute hydrochloric acid and then with water, and finally dried.
3. Ammoniacal solution of cadmium chloride : 120 gr. cadmium chloride dissolved in 1500 c.c. water, to which 600 c.c. conc. ammonia is added.
4. Iodine solution : 2.539 gr. resublimed iodine mixed with 5 gr. potassium iodide, dissolved in 100 c.c. water and made up exactly to 1000 c.c.
5. Thiosulphate solution : about 5 gr. crystallised sodium thiosulphate dissolved in 1000 c.c. water and titrated exactly against the iodine solution.

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<sup>3</sup> Ber. XXV, 2377.

## ARRANGEMENT.

The arrangement is as shown in the following figure :-

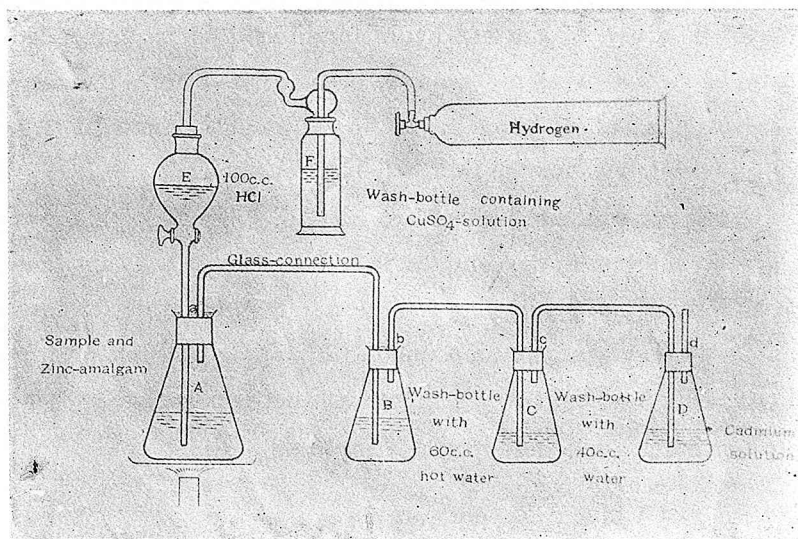


Fig. 1.

A : Hydrogen sulphide generator with a glass-stopper *a*, of which the upper side is covered with water.

E : Drop-funnel inserted into the generator A through the glass-stopper, its upper mouth being connected with a hydrogen reservoir.

B : Wash-bottle containing hot water in order not to keep hydrogen sulphide but to be able to catch as much hydrochloric acid gas as possible. Glass-connection for this and generator. Water jacket at *b*.

C : Wash-bottle, Hydrogen sulphide in this bottle, if any, must be measured and added to the main part in the next bottle. Water jacket at *c*.

D : Hydrogen sulphide absorber, which contains 10 c.c. standard cadmium solution diluted with 50 c.c. water. Water jacket at *d*.

**PROCEDURE.**

Two or three gr. of a sample crushed in pieces or in turnings and about 10 gr. of zinc amalgam are weighed into the generator A and well mixed by shaking, and the acid is then poured in from the drop-funnel. As soon as the reaction has begun to die down, a hydrogen stream is allowed to pass, which will first force in the remainder of the acid and then fill up the bottle so as to keep it air-free. Towards the end, the reaction should be quickened by application of heat. The whole operation covers about half an hour.

Practically all of the sulphur is thus converted into hydrogen sulphide. There remains in the generator neither free sulphur nor sulphuric acid : very small amounts of organic sulphides will pass over unabsorbed through the absorber. Cadmium sulphide formed is then filtered, well washed, and transferred together with the filter paper into a beaker, where it is titrated with iodine and thiosulphate.

**RESULTS.**

Results obtained with the ordinary evolution method are generally taken as too low, being often as low as nearly half of those with the gravimetric method and also of those obtained with my modification. As already remarked some of the sulphur remains in the case of the ordinary method kept either as solid in the generator, which can be detected on being fused with alkalis and tested for sulphates, or as sulphates in solution. Furthermore, some of the sulphur is then more liable to escape as organic sulphides due to the slow action of acids. Therefore a bottle containing a solution of an alkaline permanganate and connected to the absorber always shows the presence of much greater quantities of sulphates.

In spite of these facts, i. e. that the sulphur is scattered in several places, the old method is not ready to take into account anything but the results shown in the absorber. The new method is, however, to add numbers both from the absorber and the second wash-bottle

whereas those for organic sulphides are laid aside on account of their being so trifling. The following table will show clearly these relations and the comparative efficacy of both methods :—

TABLE 1.

Pig iron	Analytical method	S in Generator		S in II. wash-bottle in %	S in absorber in %	S in $\text{KMnO}_4$ solution in %	S total in %	S indicated on analysis in %
		as solid residue in %	in solution in %					
No. 1.	new	0	0	<b>0.02</b>	<b>0.30</b>	0.01	0.33	<b>0.32</b>
	old	0.03	0.05	0.01	<b>0.21</b>	0.04	0.34	<b>0.21</b>
No. 2.	new	0	0	<b>0.02</b>	<b>0.10</b>	0.01	0.13	<b>0.12</b>
	old	0.04	0.02	0.01	<b>0.06</b>	0.02	0.15	<b>0.06</b>

Experiments were then made with zinc sulphide containing 31.21%S instead of 32.85% for the pure sample, mixed with pig iron of 0.016% sulphur as determined gravimetrically, either in presence of zinc amalgam or not. The total sulphur minus that from the pig iron is compared with the theoretical number for zinc sulphide :—

TABLE 2.

Method	Mixture		S total (found) I. in gr.	S in pig iron II. in gr.	S in ZnS I-II. in gr.	S in ZnS (calc.) in gr.	S in ZnS (found) in %
	zinc sulphide in gr.	pig-iron w. 0.016%S in gr.					
	Without zinc-amalgam	0.0661 0.0628	3.2 3.2	0.0205 0.0197	0.0005 0.0005	0.0200 0.0192	0.0206 0.0196
With zinc-amalgam	0.0611 0.0633	3.2 3.2	0.0194 0.0202	0.0005 0.0005	0.0189 0.0197	0.0191 0.0197	99.00 100.00

We see that the results are better with the use of zinc amalgam and approach nearly to the theoretical number.

Comparison should now be made of the new method with the barium sulphate method. On dissolving pig iron with conc. nitric acid, some of the sulphur will be lost in the form of hydrogen sulphide, which is therefore to be caught and added to the sulphur found as barium sulphate. These are then compared with the results of my method :—

TABLE 3.

Pig iron	Gravimetric method S in %	New evolution method S in %
No. 3.	0.36 0.42 0.42 Mean : 0.40 0.41 0.38	0.40

For the same purpose, some of the standard sample<sup>4</sup> of pig iron, the Bureau of Standards, U. S. A., was analysed with the following results :—

TABLE 4.

Statements in the certificate of B. S.		New evolution method S in %
Gravimet. method S in %	Evolution method S in %	
0.049	0.038	0.05

Hence we see the new method is in all cases giving the same results as those of the gravimetric analysis.

Finally, as to the concentration of the acid, we have used that of sp. gr. 1.20 in the course of this work, but weaker acid down to sp. gr. 1.15 can safely be employed as will be seen from the following table :—

<sup>4</sup> *Vide* Circular of the Bureau of Standards, No. 25, 1922, p. 7.

TABLE 5.

With acid of sp. gr. 1.20 S in %	With acid of sp. gr. 1.15 S in %	Gravimetrically determined S in %
0.11	0.10	0.11
0.11	0.10	0.12
0.11	0.10	0.12

**SUMMARY.**

A modification of the evolution method is intended by the use of a stronger acid, sp. gr. 1.15—1.20, in presence of zinc amalgam. The results are reliable and always in accordance with those obtained gravimetrically.

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